Mechanistic aspects (SSITKA-DRIFTS) of the catalytic denitrification of water with hydrogen on Pd-Cu supported catalysts

Christodoulos P. Theologides [a], Georgios G. Olympiou [a], Petros G. Savva [a], Konstantinos Kapnisis [b], Andreas Anayiotos [b], Costas N. Costa [a,*]

[a] Department of Environmental Science and Technology, Laboratory of Environmental Catalysis, Cyprus University of Technology, P.O. Box 50329, CY 3603, Limassol, Cyprus
[b] Department of Mechanical Engineering and Materials Science and Engineering, Cyprus University of Technology, P.O. Box 50329, CY 3603, Limassol, Cyprus

ARTICLE INFO

ABSTRACT

Detailed mechanistic studies (ex-situ SSITKA-DRIFTS) have been performed on 1 wt.% Pd-0.5 wt.% Cu/γ-Al_2O_3 and 1 wt.% Pd-0.5 wt.% Cu/TiO_2-Al_2O_3 catalysts concerning the NO_3^-/H_2 and NO_3^-/H_2/O_2 reactions, in order to elucidate the promoting role of TiO_2 and O_2 in suppressing the unwanted NH_4^+ production in water media. It is demonstrated, for the first time ever, that the mechanism of N_2 production strongly depends on the nature of the support and the presence of O_2 (air) in the gas feed stream. In particular, these parameters were found to significantly affect the formation of different adsorbed active intermediate N-species on the support or/and metal (Pd, Cu) surface, providing documentary information about the signalling pathways leading to the formation of NH_4^+ and N_2. This study provides for the first time ever, an *alternative stepwise pathway* for the reduction of $NO_2^-_{(ads)}$ to $NO_{(ads)}$ and further to N_2 *on the support or metal-support interface* (metal cation sites), instead of Pd metal surface. Based on the results of the present work, it is concluded that the reduction of $NO_2^-_{(ads)}$ species is favoured on partially oxidized Pd (when adequate supply of oxygen is available). In the case of Pd-Cu/TiO_2-Al_2O_3 (NO_3^-/H_2), both adsorption and reduction of $NO_2^-_{(ads)}$ take place on the support surface leading to the formation of $NO_{(ads)}$ on TiO_2 (Ti^{4+}-NO or Ti^{4+}-NO^+), which in turns leads to enhanced N_2 production. In addition, the latter system exhibits greatly enhanced selectivity towards N_2, under oxidizing conditions, possibly due to the interaction of NO_x species (e.g., Pd-NO/N, Ti^{4+}-NO/NO^+) at the metal-support interface. On the contrary, in the absence of both titanium dioxide in the support and oxygen in the feed, the sequential reduction of $NO_3^-_{(ads)}$ takes place on different active sites of the catalyst surface, indicating that H_2 is easily dissociated on Pd particles and then spills over onto the Cu and the metal oxides (support), and secondly that $NO_{(ads)}$ is possibly diffused from the support to adjusted Pd sites, for further reaction. These mechanistic findings are very important as they reveal, for the first time ever, the active involvement of the support in the reaction mechanism and its positive effect on N_2 production.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Although several strategies have been proposed and examined to prevent unwanted release of ammonium ions (NH_4^+), as the main by-product of the hydrogenation of nitrates in aqueous media, none of them actually led to any great success. Therefore, a complete understanding of the key steps of the reaction mechanism regulating this process is critical in order to determine the main factors governing the reaction selectivity over Pd-Cu supported catalysts on various metal oxides. The mechanism of the catalytic reduction of nitrates over bimetallic Pd-Cu catalysts with H_2 has been proposed as a stepwise process consisting of two main steps: (i) hydrogenation of nitrates to nitrites on Pd-Cu clusters, where the role of the noble metal is to dissociate molecular hydrogen, thus enabling copper-nitrate reduction, and (ii) the conversion of nitrite ions to nitrogen and ammonia on Pd sites via NO intermediates [1–8]. Based on literature data [6,7], adsorbed NO on Pd is considered as the key intermediate in the production of the desired (N_2) and undesired (NH_4^+) products. Particularly, an in situ ATR-IR spectroscopic study on nitrites reduction over Pd/Al_2O_3 indicated the formation of NO on Pd surface [7]. The latter was also confirmed by Zhang et al. [1], based on $^{15}NO_2^-$ isotopic labelling

experiments coupled with a GC–MS, over Pd-In/Al$_2$O$_3$ catalyst. Many studies have been conducted to verify the potential reaction pathway towards N$_2$ in the catalytic hydrogenation of nitrates [6–8]. The formation of nitrogen via NO as the main intermediate was found to occur through several paths. Recent advances showed that N$_2$ appears to be produced by desorption-mediated reaction of NO and atomic N [9–11]. The most compelling evidence to date for N formation has been obtained from Ultraviolet Photoelectron Spectroscopy (UPS); claiming that atomic N is generated via the surface catalytic reaction of NO with H$_2$, and not through the dissociation of NO on Pd [12]. Moreover, it was found that ammonium is formed through a series of sequential reactions involving the formation of intermediate atomic N as a first step (NO + H$_2$) [13], followed by subsequent reaction of N with H [14]. However, only a few related studies [8,15] were undertaken to provide information regarding the nature and the fate of the adsorbed surface N-species formed during nitrates reduction, due to the difficulty of using such technologies (e.g., DRIFTS) in aqueous media. In this respect, Sa and Anderson [8] studied the mechanism of nitrate reduction over Pd/TiO$_2$ catalyst using infrared spectroscopy (FTIR). The IR measurements were performed with a high concentration of pre-adsorbed species and with very low water flow rates (in the form of water vapour). The reactivity of adsorbed species towards H$_2$ as determined by FTIR increases in the following order, NO$_3^-$ < NO$_2^-$ < NO. Nitrate and nitrite were found to be selectively adsorbed at Lewis acid sites on titania following exchange with OH$^-$, and reduction by Ti$_4$O$_7$ and Pd, respectively. On the contrary, NO was adsorbed on both the support and the metal, while it was reduced exclusively on Pd sites. In this case, hydrogen was dissociated on Pd, and migrated (spill over) onto the support activating the reduction of nitrates, thus indicating a strong metal-support interaction.

In previous preliminary studies it has been shown that the mechanistic pathway of nitrates reduction can be adequately traced using a modified *ex situ* DRIFTS experimental analysis [15–17]. DRIFTS studies indicated the formation of different active nitrogen containing species (in the term of reactivity) on catalyst surface (metal sites and metal-support interface) depending on the chemical composition of the support and the reaction conditions. Although DRIFTS studies were performed to assess the reactivity of intermediate N-species formed during catalytic reduction of NO$_3^-$ with H$_2$ in aqueous media, this technique by itself, cannot provide experimental proof on the actual active species formed and the elementary steps of the reaction. Such a deep fundamental understanding of catalytic reactions is of prime importance for catalyst development. Steady State Isotopic Transient Kinetic Analysis (SSITKA) has been considered as the most powerful technique in performing mechanistic studies for heterogeneous gas-solid catalytic reactions. However, up to date, no studies concerning the catalytic mechanism of aqueous nitrate reduction has been reported by using the SSITKA-DRIFTS technique. The present work aims to provide documentary information about the signalling pathways leading to NH$_4^+$ and N$_2$ production. Such information can ultimately result to better catalysts design to present high selectivity towards the desired product (N$_2$). In particular, a combined SSITKA-DRIFTS technique has been applied to study essential mechanistic aspects of the reaction at hand. SSITKA experiments, with the use of ^{15}NO$_3^-$ stable isotope, coupled with *ex situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) were conducted on 1 wt.% Pd-0.5 wt.% Cu/γ-Al$_2$O$_3$ and 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ catalysts after specific reactions conditions (100 vol.% H$_2$ or 80 vol.% H$_2$/20 vol.% air) in order to determine: (a) the chemical structure of adsorbed active and inactive (spectator) N-species, (b) the location of active N-species (metal phase or support) and (c) the fate of intermediate N-species in nitrate reduction.

It is demonstrated that essential aspects of the mechanism of N$_2$ and NH$_4^+$ formation strongly depend on the nature of the *catalyst support* and the *feed composition* as well. It was proven, for the first time, that the chemical composition of the support has a great impact on the fate of intermediate M$_{Pd or metal cation of the support}$ − NO$_x$ species (e.g., linear NO, NO$^+$), leading to the production of N$_2$ versus NH$_4^+$.

2. Experimental section

2.1. Catalysts preparation and characterization

In the present work, two bimetallic catalysts i.e., 1 wt.% Pd–0.5 wt.% Cu/γ-Al$_2$O$_3$ and 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$, were prepared and examined towards the NO$_3^-$/H$_2$ and NO$_3^-$/H$_2$/O$_2$ reactions. Coated γ-alumina spheres with 5 wt.% metal oxide (TiO$_2$) loading were prepared by immersing commercial γ-alumina spheres (d = 1.8 mm, Sasol, 604130) in a 2-propanol solution containing the desired amount of metal oxide precursor Ti[OCH(CH$_3$)$_2$]$_4$ (Aldrich). The spheres were left in solution for 24 h under mild stirring at room temperature. The impregnated alumina spheres where first dried at 120 °C and then calcined at 500 °C for 4 h prior metal (Pd and Cu) deposition. The effectiveness of the alumina-coating procedure described above and the effect of several experimental parameters on it were examined by Scanning Electron Microscopy–Dispersive X-ray (SEM–EDX) and Inductively Coupled Plasma − Mass Spectrometry (ICP–MS).

The supported bimetallic catalysts were prepared by a standard impregnation method using aqueous precursor solutions in order to obtain a palladium loading of 1 wt% and a copper loading of 0.5 wt.% Pd was initially deposited on the coated γ-alumina spheres by the incipient wetness impregnation method using Pd(NO$_3$)$_2$ (Aldrich) as precursor of palladium metal. After impregnation and drying at 120 °C, the solid samples were calcined in air at 500 °C for 4 h. The resulting monometallic solid was then impregnated with an aqueous solution of Cu(NO$_3$)$_2$ (Aldrich). After impregnation of Cu and drying at 120 °C, the resulting solid catalyst was calcined in air at 500 °C for 4 h prior use.

Scanning Electron Microscopy (SEM) studies were performed on the fresh solid catalyst after calcination. SEM analyses revealed that the above mentioned experimental procedure led to a uniform metal (Pd and Cu) distribution on alumina spheres. Pd and Cu dispersion and mean particle size were also determined by selective chemisorption of H$_2$ at 25 °C according to the following procedure: After calcination in a 20%O$_2$/He gas mixture at 500 °C for 2 h, the catalyst was reduced in H$_2$ (1 bar) at 300 °C for 2 h. The feed was then changed to He and the temperature was increased to 500 °C in He flow until no hydrogen desorption was observed. A possible H-spillover that might have taken place at 300 °C was eliminated by the latter procedure. The reactor was then quickly cooled in He flow to 25 or 200 °C and the feed was changed to a 1%H$_2$/He gas mixture for 30 min. The feed was then changed back to He and kept at 25 or 200 °C for 5 min before the temperature of the catalyst was gradually increased to 600 °C (30 deg/min) to carry out a TPD (Temperature Programmed Desorption) experiment. From the amount of hydrogen desorbed, the amount of metal (m: Pd or Cu) in the sample, and assuming H/m$_s$ = 1:1, the dispersion of metal was estimated. The actual Pd and Cu loadings (wt%) were measured by Atomic Absorption Spectroscopy (AAS) using a PG − 90 AA Spectrophotometer or Inductively Coupled Plasma − Mass Spectrometry (ICP–MS).

The specific surface area of the commercial metal oxide supports used was examined by N$_2$ adsorption at 77 K (BET method) using a multi-point Micromeritics Gemini V System.

Table 1
Sequence of steps performed for SSITKA experiments.

experiment code	sequence of step changes of liquid flow over the catalyst sample
SSITKA	$^{14}NO_3{}^-/H_2$ or $^{14}NO_3{}^-/H_2/O_2$ (25 °C, 150 min) $\rightarrow$ $^{15}NO_3{}^-/H_2$ or $^{15}NO_3{}^-/H_2/O_2$ (25 °C, 150 min)
A	H
	e (25 °C, 50 cc/min) $\rightarrow$ DRIFTS (5, 10, 15, 30, 45, 60 min) $\rightarrow$ He (500 °C, 15 min, 50 cc/min) $\rightarrow$ cool quickly to room temperature under He (25 °C, 50 cc/min) $\rightarrow$ background spectrum IR
B	background spectrum IR

2.2. Catalytic process

The implementation of the catalytic studies performed in the present work requires the use of a special flow apparatus, which is suitable for three-phase catalytic experiments (solid-liquid-gas). Catalytic experiments were conducted in a custom-built autoclave CSTR reactor (Autoclave Engineers, U.S.A., and PID Eng &Tech, Spain) equipped with a Mahoney-Robinson catalyst basket (200 mL). The catalyst basket and the reactor's inlets and outlets have been specially designed in order to maximize the contact region between the three phases and to minimize possible external mass transport phenomena. All catalytic experiments were performed in a continuous flow system: the solid phase was stationary, whereas the liquid (nitrates solution) and the gas-phase reducing medium (hydrogen/helium or hydrogen/air gas mixture) were under continuous flow at about 1 atm total pressure and 25 °C. The reactor system was equipped with a mechanical stirrer, probes for temperature and pressure control, and inlet-outlet ports for sampling and addition of liquids and gases. Four thermal mass-flow control valves run by a controller were used in order to *in situ* prepare a given gas mixture. An HPLC Pump equipped with a manometric module was used in order to succeed a constant flow of the liquid phase (nitrates aqueous solution). The whole system was controlled by a programmable software.

All experiments were conducted in the three-phase continuous flow stirred tank reactor as described above. The volume of the liquid phase (180 mL), the initial nitrate concentration in the liquid phase (75 mg/L) (use of HNO_3 solution), the liquid flow rate (4 mL/min), the mass of catalyst (4.0 g), the flow rate of gas feed stream (100 NmL/min), the gas feed stream composition (80 vol.% H_2 and 20 vol.% air) and the stirrer's rotation speed (400 rpm) were kept constant in all catalytic experiments, except in those where a specific parameter was under examination. The nitrates solution was prepared by dissolving an appropriate amount of concentrated nitric acid in deionised water in order to form the desired initial concentration of nitrates. All catalytic experiments were repeated in triplicate in order to assure reproducibility of results.

Prior each catalytic reaction, a start-up procedure was applied. Initially catalysts were in-situ calcined in air at 500 °C for 2 h, followed by reduction of the catalytic active phase with pure H_2 (1 bar) at 300 °C for 2 h. The reactor was then quickly cooled in He flow to 25 °C. The start-up procedure was completed by introducing 180 mL of the desired nitrate solution in the reactor tank which was kept at constant temperature (25 °C) and under He flow (100 mL/min) in order to achieve a constant pressure of 1.2 atm. A liquid micro valve was immediately automatically opened while the liquid pump was set to 4 mL/min keeping the volume inside the tank constant. At the same time the reducing gas feed (H_2 or H_2/O_2) was automatically introduced at the desired flow rate in order to activate the reaction (or just He for $NO_3{}^-$ adsorption). The liquid flow rate remained stable approximately at 4 mL/min during the whole process. Samples were periodically taken from the outlet of the reactor to analyze the concentration of $NO_3{}^-$, $NO_2{}^-$ and $NH_4{}^+$ after 0.45 mm filtration.

According to the literature [6–9], the possible gaseous products of the catalytic reduction of nitrate ions are expected to be NH_3, N_2, N_2O, NO and NO_2, whereas in the liquid phase the possible products are $NH_4{}^+$, $NO_2{}^-$, as well as unreacted nitrate ions ($NO_3{}^-$). Quantitative analysis of the liquid phase at the reactors outlet was performed by UV–vis spectrophotometry (Spectroquant® Pharo 300). Suitable UV-kits (Merck Spectroquant® test kits) were used for the determination of $NO_3{}^-$, $NO_2{}^-$ and $NH_4{}^+$. Each sample was analysed in triplicate in order to reduce/eliminate possible measurement errors. The gaseous product mixture of the reaction was analysed using an on-line quadrupole Mass Spectrometer (MS), as well as gas analysers for nitrogen oxides (NO_x and N_2O). Suitable mass balances were used for the indirect determination of the concentration of the reaction products that could not be determined directly (e.g., N_2).

2.3. FTIR and SSITKA studies

Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectra were recorded on a Perkin-Elmer Spectrum 100 spectrophotometer with the use of a high temperature/high-pressure temperature controllable DRIFTS cell (Praying Mantis™ Diffuse Reflectance Attachment, Harrick Scientific) equipped with ZnSe windows. About 40 mg (sample/KBr = 1:1) of catalyst sample in fine powder form were used. It is noted that the possible effects of the presence KBr on the quality of the spectra obtained has been carefully examined in the present work. Samples with and without KBr dilution were examined (at the highest and lowest temperature used in the present DRIFTS studies). It was found that KBr does not influence the spectra in terms of the number and position (wavenumber) of the peaks observed. No additional peaks are observed when the samples are diluted in KBr. The only advantage when using KBr was that the spectra present more sharp and distinct peaks. The above consist a strong evidence/proof that KBr can be considered as an inert material, at least under the conditions examined in the present work. After reaction ($NO_3{}^-/H_2$ or $NO_3{}^-/H_2/O_2$) or $NO_3{}^-$ adsorption at 25 °C, the catalyst samples were dried at room temperature in a desiccator and then were placed in the DRIFTS cell sample holder. The total gas flow rate (He or H_2) applied in the DRIFTS cell was 50 NmL/min. For FTIR single-beam background subtraction, the spectrum of the catalyst solid in the absence of any adsorbed nitrates was taken in N_2 flow. FTIR spectra were collected under He or H_2 (gas phase) at the rate of 1 scan/s and at 2 cm^{-1} resolution in the 800–2400 cm^{-1} range under different temperatures (25, 100, 200, 400, 500 °C) for various times (0, 5, 10, 15, 30, 45, 60 min). The averaged spectrum (40 spectra were collected) was then recorded. Spectra were analyzed by using the instrument's Spectrum for Windows software (Perkin-Elmer).

SSITKA experiments involved the switch of the aqueous feed from $^{14}NO_3{}^-$ mixture to an equivalent isotopic $^{15}NO_3{}^-$ mixture, after steady state was achieved. Table 1 illustrates the necessary sequence of steps (SSITKA $\rightarrow$ A or B) followed for each kind of isotopic transient experiment conducted.

3. Results and discussion

3.1. Catalysts characterization

Physicochemical characterization of solid catalysts involved the in-depth study of both the bulk and the surface of the catalysts before and after the reaction. The metal (Pd, Cu and Ti) content of the examined catalysts (Pd–Cu/γ-Al$_2$O$_3$ and Pd–Cu/TiO$_2$-Al$_2$O$_3$) was determined either by using Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma–Mass Spectrometry (ICP–MS). The chemical analysis showed that most of the metal precursor salts were actually deposited on the support. In particular Pd loading was found to vary in the 0.75-1.0 wt.% range, whereas Cu loading was found to be between 0.35 and 0.5 wt.%. SEM-EDX analyses revealed that Pd and Cu were uniformly distributed at the outer surface of alumina spheres. The dispersion of Pd and Cu (as total metal) was found to vary between 0.35 and 0.4 for both catalysts. The average particle size for Pd and Cu clusters was found to be in the area of 3.7-4.5 nm. Despite the relatively low loading of TiO$_2$ achieved (4–5 wt.%), the coverage of γ-Al$_2$O$_3$ spheres was found to be adequate and uniform as proven by SEM-EDX analyses.

The specific surface area of the examined catalysts was found to be 84 and 81 m^2/g for Pd–Cu/γ-Al$_2$O$_3$ and Pd–Cu/TiO$_2$-Al$_2$O$_3$, respectively.

3.2. Catalytic studies

The catalytic activity and selectivity of 1 wt.% Pd–0.5 wt.% Cu/γ-Al$_2$O$_3$ and 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ catalysts were examined towards the NO$_3^-$/H$_2$ and NO$_3^-$/H$_2$/O$_2$ reactions. Fig. 1 presents the effect of the support and feed stream composition on the catalytic activity (Fig. 1a) and selectivity (Fig. 1b) of the reaction at hand. As shown in the comparative results presented in Fig. 1, significant shifts were observed between the two catalysts examined, particularly in case of NH$_4^+$ selectivity (Fig. 1b). As seen in Fig. 1, Pd–Cu/TiO$_2$-Al$_2$O$_3$ catalyst was found to be highly active for nitrate conversion ($X_{NO_3^-}$, %). In particular, the catalytic activity towards NO$_3^-$ of Pd–Cu/TiO$_2$-Al$_2$O$_3$ ($X_{NO_3^-}$ = 83%) was found to be slightly higher than that obtained on Pd–Cu/γ-Al$_2$O$_3$ ($X_{NO_3^-}$ = 74%). The comparative results presented in Fig. 1 also indicate that the reaction selectivity towards NH$_4^+$ is clearly affected by the support chemical composition. In more detail, significantly lower NH$_4^+$ selectivity value (by 55%) was obtained over Pd–Cu/TiO$_2$-Al$_2$O$_3$ compared to Pd–Cu/γ-Al$_2$O$_3$.

The effect of the presence of oxygen in the reaction's feed stream on the catalysts behaviour towards the reduction of nitrates with hydrogen using a continuous flow setup, was studied in a previous work of our group [17]. Within the present work, a series of mechanistic experiments were conducted in order to determine the intrinsic reasons that lead to the abovementioned behavior.

3.3. Catalyst surface reactivity studies by ex-situ DRIFTS

3.3.1. An overview study of N-species

A series of FTIR experiments using a DRIFTS cell were performed, in order to elucidate the promoting role of TiO$_2$ and O$_2$ in reducing the unwanted NH$_4^+$ production in the NO$_3^-$/H$_2$ reaction. The chemical structure of the possible adsorbed intermediate N-species formed on the surface of 1 wt.% Pd–0.5 wt.% Cu/γ-Al$_2$O$_3$ and 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ catalysts during NO$_3^-$/H$_2$ and NO$_3^-$/H$_2$/O$_2$ reactions at 25 °C was studied.

It should be pointed out that the removal of the aqueous phase (during the ex-situ DRIFTS studies of the present work) might have caused some consequences on the structure/nature of the species formed during actual reaction conditions. Unfortunately,
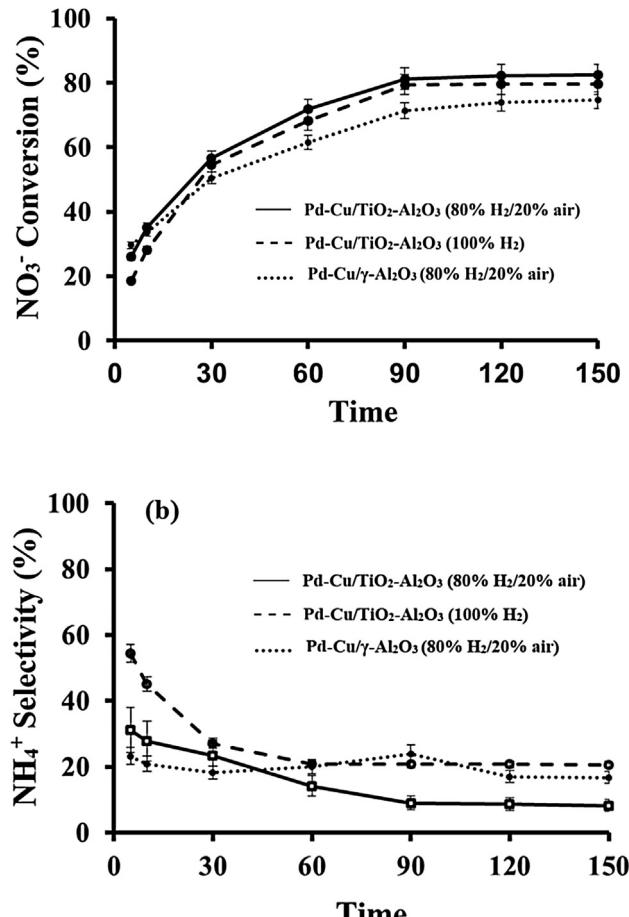

Fig. 1. Nitrates conversion (a) and selectivity towards NH$_4^+$ (b) as a function of reaction time obtained over Pd-Cu/Al$_2$O$_3$ and Pd-Cu/TiO$_2$-Al$_2$O$_3$ catalysts after 2.5 h of continuous reaction. Reaction conditions: Gas Feed Stream Composition = 100 vol.% H$_2$ or 80 vol.% H$_2$/20 vol.% air; [NO$_3^-$]° = 75 mg/L; Liquid Flow Rate = 4 mL/min; W$_{cat}$ = 4 g; T = 25 °C; P = 1.2 atm.

this is an unavoidable weakness of the ex-situ studies performed in the present work, since in-situ DRIFTS studies are not feasible. Nevertheless, quite safe conclusions can be drawn by comparing the results obtained (spectra) on different samples that have been examined under exactly the same experimental conditions (apart from the parameter under investigation).

In addition, our results obtained after examining samples that have been dried under different drying protocols showed that the presence of the aqueous face does not appear to influence the nature (wavenumber) of the species observed but it only affects the shape of the peaks and resolution of the spectra obtained. In addition, the presence of liquid on the catalysts' surface completely destroys the resolution of spectra in the range of 1400–1800 cm^{-1}, because of the very broad absorption band of adsorbed water.

Studies regarding the effect of water (vapor) on the species formed after adsorption of NO/NO$_2$ on NSR catalysts report that the addition of water in the feed either does not affect at all the species formed (same FTIR or DRIFTS spectra before and after vapor addition) or might cause the conversion of nitrates to "ionic" species [18–20]. Since in our catalytic experiments water was always present during reaction, one can expect that both nitrate and ionic species should have been formed on the catalyst's surface. Indeed, this is something that was proved by our DRIFTS studies. Since both nitrate and ionic (1395 cm^{-1}) species were observed in our studies, it can be claimed that the removal of the aqueous phase does not

Table 2
Absorption bands of various adsorbed N- species on supported Pd catalysts.

| Species	Wavenumber (cm^{-1})
gas N_2O (only when surface exposed to nitrite not to nitrate)	2240–2212
nitrosyls (NO^+ και NO_2^+) on metal oxide support	2200–2000
adsorbed water on support (combination stretching mode, v_2 + libration), $N\equiv N$ stretching vibrations if azide type species (N_3) are formed from nitrate reduction	2130
nitrosyls (NO^+) on ionic forms of Pd	1880–1780
adsorbed NO on Pd $^{n+}$	1837–1782
nitrosyls (NO^+) on Pd	1750–1730
linearly bound (adsorbed) NO on Pd (100)	1744, 1720, 1707
NO on Pd$\circ$ (111)	1742
dinitrosyl complex (NO^+)	1710
bridging nitrosyls (NO^+) on Pd$\circ$(Pd–NO^-)	1670–1640 (1655), 1570
bidentate nitrates and molecularly adsorbed water (bending stretching mode, v_2) on support,	1640–1620
symmetric deformation of NH_3 coordinated to exposed Lewis acid sites (Ti^{4+}-NO/NOH)	1602
$N\equiv O$ stretching mode of bidentate nitrate, Ti–O_2NO	1550
bidentate nitrates on support (Al_2O_3, TiO_2)	1540–1530
unidentate nitrates on support	1510
bidentate nitrates on support or metal- support surface	1472, 1435, 1360
unidentate nitrates on Pd	1470
NH_4^+ on bronsted acid sites on TiO_2	1456, 1441,1420
a symmetric N—O stretching mode of bidentate nitrate, Ti–O_2NO	1301 (as a shoulder)
N-species on support	1410
ionic nitrates on Cu cations	1395
nitrates, Nitro NO_2 – chelating on support	1251
coordinated nitrates on support	200–1100, 1050
coordinated to exposed Lewis acid sites (Ti^{4+}-NO/NOH)	1164, 1160
bridgings NO_2^- on support (Al_2O_3)	1130
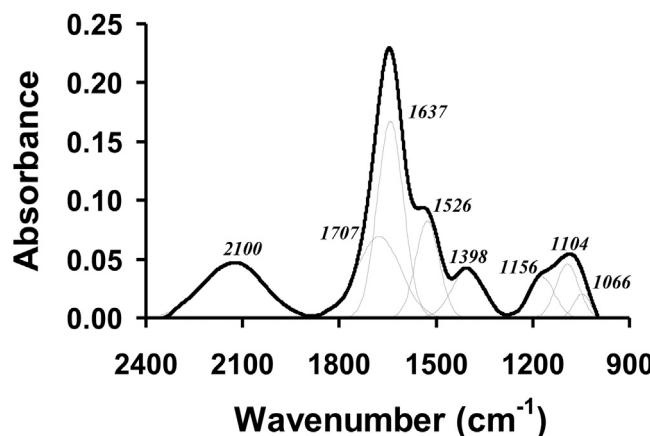
Fig. 2. Deconvolution of typical DRIFTS spectrum recorded in the 2400–1000 cm^{-1} range over supported Pd-Cu catalyst after NO_3^- absorption. Reaction conditions: Gas Feed Stream Composition = 100 vol.% He; TPD Flow Rate = 50 NmL/min; $[NO_3^-]^\circ$ = 75 mg/L; Liquid Flow Rate = 4 mL/min; W_{cat} = 4 g; T = 25 °C; P = 1.2 atm.

affect significantly the nature of adsorbed species on the catalyst's surface.

Fig. 2 shows a representative DRIFTS spectrum recorded in the 2400–1000 cm^{-1} range over Pd-Cu/Al_2O_3 after NO_3^- absorption at 25 °C. As shown in Fig. 2, the dencovolution (OriginPro) of the spectrum in the region of 2400–1000 cm^{-1} leads to the resolution of additional peaks. The overlapping of the peaks of different adsorbed N-species, as well as the species low concentration on the surface of the catalyst can affect the appearance of the spectrum.

The assignment of the various IR absorption bands was made based on bibliography data [8,21–47]. Table 2 provides an overview of the chemical structure and the respective IR absorption frequency (stretching mode) for various adsorbed N-species reported in the literature, some of which are found in the DRIFTS spectra of the present work. The first main peak (highest frequency) observed in the region of 2200–2000 cm^{-1} (max at ~2100 cm^{-1}) corresponds to nitrosyls (NO^+) adsorbed on metal cations of the support. The latter band could be also attribute to azide species

on the support [8,21,22]. In the experiments performed by Hadji-ivanov et al. [23] and Ramis et al. [24] using TiO_2-V_2O_5 and TiO_2 catalysts after NO_2^- adsorption, this same peak was observed in the region of 2200–2000 cm^{-1}. According to the authors, this peak may either correspond to nitrosyls, NO^+ adsorbed on oxygen vacant places, which are intermediate species of atomic nitrogen after the reduction of adsorbed NO_2^- to NO, or to the adsorption of two molecular species of NO_2 on active sites of Ti^{4+}-O_2 [23–28]. The appearance of a peak in higher frequencies, more specifically in the region of 2240–2212 cm^{-1} is due to the N_2O gas (not appeared in the present work) [8,29]. The broad complex of bands observed in the 1850–1350 cm^{-1} region deserves special attention for the reaction under investigation. Adsorbed NO, nitrates, nitrites and NH_x species formed on the support and on the metal surfaces (Pd and/or Cu) during the reaction, all absorb in this region of the IR spectrum. According to the literature, the peaks corresponding to adsorbed NO on Pd appear usually in the region of 1880–1680 cm^{-1}. The peak in the region of 1880–1780 cm^{-1} corresponds to adsorbed nitrosyls (NO^+) on Pd [23], the peak in the region of 1837–1782 cm^{-1} represents NO adsorbed on oxidized Pd atoms [30], the peak in the region of 1750–1730 cm^{-1} is attributed to NO adsorbed on Pd^0 (Pd-NO) [30], the peaks at 1744, 1720 and 1707 cm^{-1} represent linear NO species adsorbed on Pd [8,23,26,31–35], the peak at 1710 cm^{-1} represents dinitrosyl complex [32,34–36], and the peak in the region of 1670-1640, as well as the peak at 1570 cm^{-1}, represent bridging NO^+ on Pd$\circ$ [30,32–34]. The peak in the region of 1640–1620 cm^{-1} is due to both molecular water adsorbed on the support and adsorbed nitrites on Pd [8,23,24,35–40], whereas the peak at 1610 cm^{-1} is attributed to the asymmetrical distortion of NH_3 due to exposed Lewis acidic sites of TiO_2 [8,38,41]. The peak at 1530 cm^{-1} is probably due to adsorbed nitrites with the participation of either the support or the interface of metal and support [23,42]. Moreover, nitrites adsorbed on TiO_2 have been reported in the regions of 1550, 1472, 1435, and 1360 cm^{-1} [8,33,35–37]. Within the same region (cm^{-1}) the peaks at 1456 and 1441 cm^{-1} are reported to correspond to adsorbed NH_4^+ on Bronsted acid sites on TiO_2 [8,23,44–46]. Adsorbed unidentate nitrates on the support [38,44,46] and the Pd [43] usually give peaks at 1510 and 1470 cm^{-1}, respectively.

The peak appearing at 1395 cm^{-1} is common for all Cu supported catalysts and corresponds to ionic nitrates adsorbed on Cu cations [8,41]. The weak absorption peak at 1251 cm^{-1}, which is rarely clearly distinguished from the two strong peak complexes that surround it, is due to the various nitric species that are adsorbed on the support, as well as to chelating nitrites that are formed during the reaction with the support. The latter are usually inactive species of the reaction [47]. The broad complex of peaks that is observed in the region of 1200–1000 cm^{-1} is attributed mainly to the existence of adsorbed N-species on the support. The peak that appears in the region at 1164–1160 cm^{-1} corresponds to NO/NOH species adsorbed on acidic Lewis positions of TiO$_2$ (Ti^{4+}-NO/NOH) [8,38,41]. The peak at 1130 cm^{-1} is due to adsorbed bridging nitrites on Al$_2$O$_3$, whereas the peak at 1050 cm^{-1} corresponds to various compounds of coordinated nitrates [39].

The identification of the various intermediate adsorbed N-species which were formed on the surface of the examined catalyst during nitrate reduction was based on their position (absorption wavelength) (see Table 2).

3.3.2. Reactivity of adsorbed N-species that are formed during the NO$_3^-$/H$_2$/O$_2$ reaction

The reactivity of adsorbed nitrate species and their intermediate products, formed during the NO$_3^-$/H$_2$/O$_2$ reaction on 1 wt.% Pd-0.5 wt.% Cu/γ-Al$_2$O$_3$ and 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$, with hydrogen, was studied. This essential mechanistic information contributes towards the understanding of the mechanisms involved in the complicated catalytic reduction of nitrates. According to the literature (see Table 2), the reduction of nitrates to the final products of NH$_4^+$ and N$_2$, proceeds through multiple intermediate N-species, the identification of which is achieved using IR spectroscopy (FTIR).

The results obtained over the examined catalysts are presented in Fig. 3. As illustrated in Fig. 3, NOH (1173 cm^{-1}) appear to react with hydrogen. The latter species might be intermediate products of the reduction of nitozyls (NO$^+$) (2110 cm^{-1}) on the support and possible precursor of ammonium ions. The surface coverage of this species can be considered as essential information for the selectivity of the reaction towards ammonium ions. In addition, the surface coverage of adsorbed nitrites on support (1529 cm^{-1}), as well as ionic nitrates on the Cu (1397 cm^{-1}) showed a remarkable decrease when reacted with hydrogen. NO$_3^-$ adsorbed on Cu (peak at 1397 cm^{-1}) show the highest reactivity towards hydrogen at 25 °C. Several studies show evidence of the dissociative adsorption of H$_2$ on Pd and the diffusion of atomic hydrogen from the Pd metal surface to Pd-Cu crystallites through spill over. After Hydrogen (H$_2$) splits to atomic H and chemisorbs on the surface of Pd, it moves through spill over to the Cu crystallites (bimetallic Pd-Cu positions), where the activation of the surface reaction of the nitrates will take place [48–57]. However, several studies have also reported the reduction of nitrates by monometallic supported catalysts (Pd/CeO$_2$, Pd/SnO$_2$, Pd/TiO$_2$) [8,58–61]. These studies support the view of the involvement of the support in the reduction mechanism of nitrates. The reduction of intermediate N-species (NO$_3^-$, NO) that are formed on the support near the interface of Pd (e.g. adsorbed bidentate nitrates on the support) is directly dependent on the ability of the atomic hydrogen to be dispersed from Pd clusters to the support. The reduction of N-species, which appear close to the interface between the metal and the support, proceeds through the dispersion of the adsorbed hydrogen to Pd. The dispersion of hydrogen on the support surface is energetically difficult beyond a certain distance from the Pd crystallites. In mechanistic SSITKA-MS and SSITKA-DRIFTS studies of the H$_2$-SCR reaction of NO on a Pt/MgO-CeO$_2$ catalyst, it was found that only chemisorbed H species of the support that are within a small region around the Pt crystallites are involved in the mechanism of the reaction [62,63].
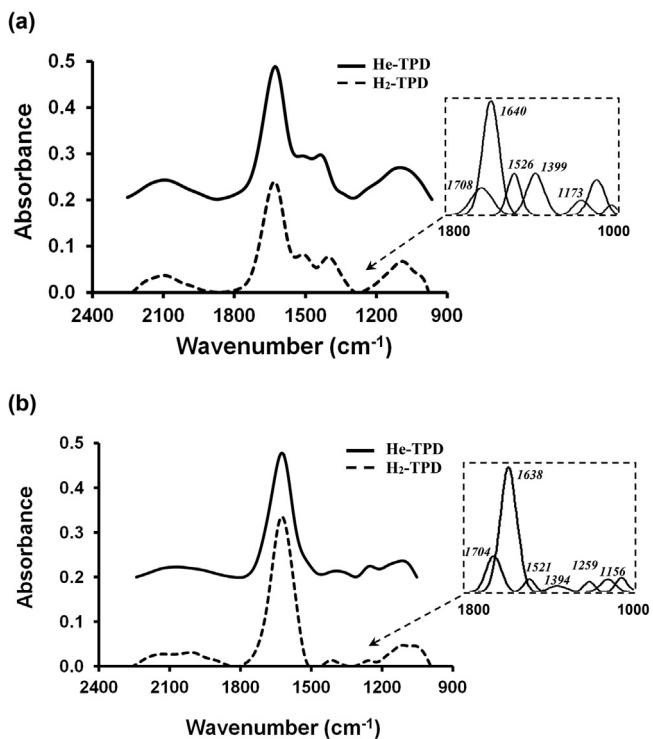

Fig. 3. DRIFTS spectra obtained over the 1 wt.% Pd-0.5 wt.% Cu/γ-Al$_2$O$_3$ catalyst (a) and the 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ catalyst (b) after NO$_3^-$/H$_2$/O$_2$ reaction, and temperature programmed desorption (TPD) under He (—) or H$_2$ (—) at 25 °C. Deconvolution of the DRIFTS spectra recorded in the 1800–1100 cm^{-1} range in each case. Reaction conditions: Gas Feed Stream Composition = 100 vol.% H$_2$ or 80 vol.% H$_2$/20 vol.% air; TPD Flow Rate = 50 NmL/min; [NO$_3^-$]$^\circ$ = 75 mg/L; Liquid Flow Rate = 4 mL/min; W$_{cat}$ = 4 g; T = 25 °C; P = 1.2 atm.

In situ FTIR studies that were performed on a Pt/La-Ce-MnO catalyst showed the existence of two active intermediate species, one of which absorbs in the region of 1500–1550 cm^{-1} [47]. According to the literature [27,63], the latter was found to correspond to adsorbed nitrites, for the formation of which a metal cation of the support and a Pt atom or two metal cation of the support that are very close to Pt crystallites. According to the above, it is obvious that in this case the nitrites adsorbed on support sites close to Pd, while the more reactive ionic nitrates are adsorbed on bimetallic Pd-Cu sites. It must be noted that the reactivity of the adsorbed nitrites on Pd cannot be clearly examined since the peak overlaps with that of the adsorbed molecular water, as mentioned before. However, comparing the spectra recorded for each case (Fig. 3a and b), some very important information arise, regarding the reactivity of these specific species. In this respect, adsorbed species on Pd (peak at 1637 cm^{-1}) showed increased reactivity after the reaction of NO$_3^-$/H$_2$/O$_2$ compared with adsorbed species on the support (peak at 1529 cm^{-1}).

3.3.3. Identification of the chemical structure of active adsorbed active N-species of the NO$_3^-$/H$_2$ and NO$_3^-$/H$_2$/O$_2$ reactions over 1 wt.% pd–0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ and 1 wt.% Pd–0.5 wt.% Cu/γ-Al$_2$O$_3$ with the use of SSITKA-DRIFTS technique

Steady State Isotopic Transient Kinetic Analysis (SSITKA) has been applied in order to gain more fundamental information concerning key aspects of the mechanism of nitrates reduction with hydrogen. This technique combined with DRIFTS can lead to the identification of the structure and chemical composition of the active intermediate species involved in the reaction mechanism that ultimately result to the formation of the final products (N$_2$ and NH$_4^+$). In particular, an attempt was made to identify the various active and inactive N-species which are formed on the sur-

Table 3
Height ratios (with respect to the peak at 1397 cm^{-1}) of the DRIFTS peaks observed over supported-Pd-Cu catalysts for the NO_3^-/H_2 and $NO_3^-/H_2/O_2$ reactions (based on Fig. 6b).

Catalyst	Reaction	Wavenumber (cm^{-1})					
		2100	1708	1640	1521	1397	1170
		Height Ratio					
Pd-Cu/Al$_2$O$_3$	NO_3^-/H_2	1.01	1.38	3.42	1.73	1	0.92
Pd-Cu/Al$_2$O$_3$	$NO_3^-/H_2/O_2$	1.26	1.41	3.96	1.68	1	1.51
Pd-Cu/Al$_2$O$_3$-TiO$_2$	NO_3^-/H_2	1.13	1.05	3.31	0.11	1	1.41
Pd-Cu/Al$_2$O$_3$-TiO$_2$	$NO_3^-/H_2/O_2$	1.40	1.06	4.23	0.03	1	1.83

(a)

(b)
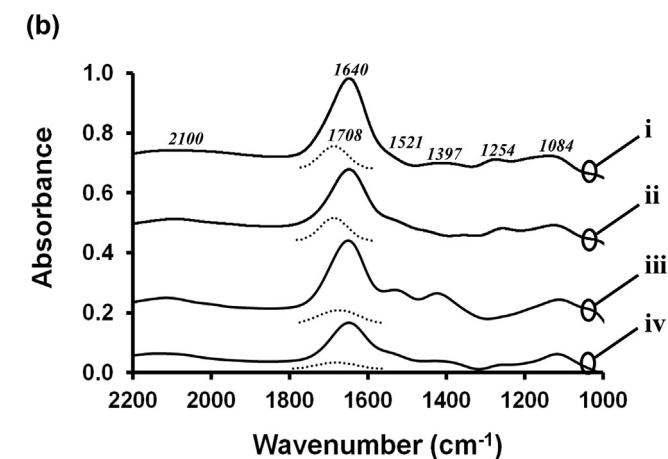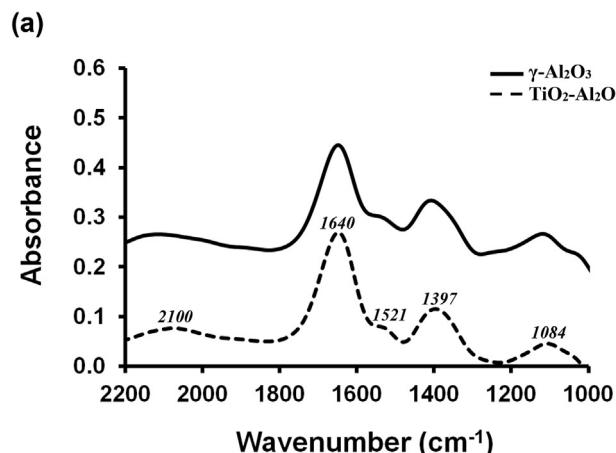
Fig. 4. DRIFTS spectra obtained over 1 wt.% Pd-0.5 wt.% Cu/γ-Al$_2$O$_3$ (—) and 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ (—) catalysts after NO$_3^-$/He absorption (a) or NO$_3^-$/H$_2$ and NO$_3^-$/H$_2$/O$_2$ reactions (b), and temperature programmed desorption (TPD) under He or H$_2$ at 25 °C. i: TiO$_2$-Al$_2$O$_3$ (NO$_3^-$/H$_2$/O$_2$); ii: TiO$_2$-Al$_2$O$_3$ (NO$_3^-$/H$_2$); iii: γ-Al$_2$O$_3$ (NO$_3^-$/H$_2$/O$_2$); iv: γ-Al$_2$O$_3$ (NO$_3^-$/H$_2$). Reaction conditions: Gas Feed Stream Composition = 100 vol.% H$_2$ or 80 vol.% H$_2$/20 vol.% air; TPD Flow Rate = 50 NmL/min; [NO$_3^-$]° = 75 mg/L; Liquid Flow Rate = 4 mL/min; W$_{cat}$ = 4 g; T = 25 °C; P = 1.2 atm.

Fig. 5. The DRIFTS spectra obtained over 1 wt.% Pd-0.5 wt.% Cu/γ-Al$_2$O$_3$ and 1 wt% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ catalysts after ^{14}NO$_3^-$/H$_2$ or ^{14}NO$_3^-$/H$_2$/O$_2$ reaction, and temperature programmed desorption (TPD) under He at 25 °C, that will be compared with DRIFTS spectra observed after ^{15}NO$_3^-$/H$_2$ or ^{15}NO$_3^-$/H$_2$/O$_2$ reaction, respectively.

sequence of steps followed in the present work, for each kind of isotopic transient experiment conducted, is reported in Table 1.

Fig. 6 presents the DRIFTS spectra obtained over 1 wt.% Pd-0.5 wt.% Cu/γ-Al$_2$O$_3$ and 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ catalysts, under He, after ^{14}NO$_3^-$/H$_2$ or ^{14}NO$_3^-$/H$_2$/O$_2$ reaction at 25 °C. These spectra were used as reference against the spectra taken after ^{15}NO$_3^-$/H$_2$ or ^{15}NO$_3^-$/H$_2$/O$_2$ reaction, respectively, for the identification of the active intermediate N-species (Fig. 4).

As shown in Fig. 5, six peaks are observed in all the spectra obtained, which correspond to different adsorbed nitrogen containing species. Each of the peaks was assigned to the corresponding N-species based on literature data (see Table 2). The IR spectra obtained with the Pd-Cu/Al$_2$O$_3$ catalyst after NO$_3^-$/H$_2$/O$_2$ and NO$_3^-$/H$_2$ reactions appear to be similar, except for some quantitative differences. The quantitative differences of the two spectra can only be accurately evaluated after proper normalization of the various peaks obtained. Table 3 reports the height ratios of the main peaks presented in the spectra of Fig. 6 (as compared to the height of the at 1397 cm^{-1}).

Based on the results of Table 3 and Fig. 5, two distinct differences are observed when oxygen was present in the reaction's feed stream. In particular, peaks at 1642 and 2100 cm^{-1}, cm^{-1}, corresponding to adsorbed nitrites on Pd°, and to nitrozyls (NO$^+$) on the support (or the metal-support interface), respectively, appear relatively increased. The increase of adsorbed nitrites on Pd can be explained by the partial oxidation of Pd metal associated with applied oxidizing conditions. Based on the latter results, it can be claimed that adsorbed nitrites on Pd and nitrozyls on the support lead selectively to the production of N$_2$ and thus, the enhancement of these species (by oxygen gas) is expected to favor the reaction selectivity towards N$_2$, a fact that is supported by the catalytic results obtained over the present catalysts. This is further supported by the fact that nitrozyl species have been reported as candidate precursor intermediates for nitrogen formation (e.g., through the formation of NOH) [8]. The latter hypothesis is further evidenced by the fact that the relative height of the peak at 1170–1160 cm^{-1} also increases when oxygen is present in the feed

face of 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ and 1 wt.% Pd–0.5 wt.% Cu/γ-Al$_2$O$_3$ catalysts during NO$_3^-$/H$_2$ or NO$_3^-$/H$_2$/O$_2$ reaction at 25 °C. These various N-species, adsorbed on the catalysts surface, can either participate (*active species*) or not participate (*inactive species or spectators*) in the mechanistic pathways that lead to the formation of the final products. The discrimination between active and inactive species can only be performed by using isotopic labeling techniques such as SSITKA. After 120 min of ^{14}NO$_3^-$/H$_2$ (or ^{14}NO$_3^-$/H$_2$/O$_2$), the aqueous feed stream was switched to ^{15}NO$_3^-$/H$_2$ (or ^{14}NO$_3^-$/H$_2$/O$_2$), simultaneously exchanging the reversibly chemisorbed N-species with ^{15}N isotope. The necessary

Fig. 6. Influence of temperature on N-species adsorbed on 1 wt.% Pd-0.5 wt.% Cu/γ-Al$_2$O$_3$ (a) and 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ (b) catalysts after NO$_3^-$/H$_2$ (1) and NO$_3^-$/H$_2$/O$_2$ reactions (2), and temperature programmed desorption (TPD) under He at 25 °C. Spectra recorded in the 2400–1000 cm^{-1} range after 25, 50, 100, 300, 400, 500 °C under flow of He (TPD). Reaction conditions: Gas Feed Stream Composition = 100 vol.% H$_2$ or 80 vol.% H$_2$/20 vol.% air; TPD Flow Rate = 50 NmL/min; [NO$_3^-$]° = 75 mg/L; Liquid Flow Rate = 4 mL/min; W$_{cat}$ = 4 g; T = 25 °C; P = 1.2 atm.

(seen after deconvolution). The latter peak is attributed to adsorbed NOH species (1165 cm^{-1}) on the support, which are most probably produced by the hydrogenation of nitrozyl species and may ultimately lead to nitrogen production.

These observations are directly related to the selectivity of the NO$_3^-$/H$_2$ reaction and greatly support the catalytic results obtained over the same catalysts regarding the inhibitory effect of oxygen on the formation of ammonium ions. According to these catalytic studies, the presence of oxygen in the gas feed stream significantly decreases the selectivity of the reaction towards ammonia. Moreover, Temperature Programmed Surface Reaction (TPSR) studies, recently performed on the aforementioned catalysts after NO$_3^-$/H$_2$ reaction, have shown significantly increased concentration of desorbed NH$_3$ or ammonium surface species (C$_{NH3}$ = 19.2 μmol/g), compared to the amount of the same species obtained after NO$_3^-$/H$_2$/O$_2$ reaction (C$_{NH3}$ = 0.7 μmol/g).

The most significant difference observed when TiO$_2$ was used as a coating material of Al$_2$O$_3$ spheres is the abrupt decrease (or even elimination) of the peak at 1520 cm^{-1} (Fig. 5), which corresponds to adsorbed nitrites on the support (or the metal-support interface). As seen in Fig. 5, the latter peak presents a very large decrease in the IR spectrum obtained with Pd-Cu/Al$_2$O$_3$-TiO$_2$ after NO$_3^-$/H$_2$ reaction, while it is almost absent in the spectrum obtained after NO$_3^-$/H$_2$/O$_2$ reaction. The latter result signifies the importance of the support chemical composition on the overall behavior of supported Pd-Cu catalysts towards the reduction of nitrates with

hydrogen in aqueous media. As recently reported [21,22], the Pd-Cu/Al$_2$O$_3$-TiO$_2$ catalyst was found to be more selective towards N$_2$, compared to Pd-Cu/Al$_2$O$_3$. Based on the above considerations, it's reasonable to assume that adsorbed nitrites on the support may lead selectively to the formation of NH$_4^+$ during the hydrogenation reaction. A similar behavior (but less intense) is also observed in the case of the peak at around 1690 cm^{-1}, which correspond to linear NO on Pd metal. As seen in Table 3, the relative peak height of these species is reduced when TiO$_2$ is used as a coating material of Al$_2$O$_3$. This is a result of great significance, indicating that the chemical composition of the support may also play an important role on the state (oxidation state) of the metallic phase (e.g., via metal-support interactions). Moreover, according to the results of Table 3, the surface coverage of nitrozyls (NO$^+$) on the support (2100 cm^{-1}) seem to slightly increase when TiO$_2$ is present in the support system. As mentioned above the latter species is believed to be the key intermediate that leads to nitrogen formation during the hydrogenation of nitrates. This argument is strongly supported by the catalytic and TPSR results obtained over the present catalysts, where it was found that titanium dioxide has an inhibitory effect on the formation of ammonium ions.

Finally, the slight increase of the relative peak height at 1170 cm^{-1} (attributed to NOH species on the support), when TiO$_2$ is added to the support, indicates that these species are probably formed after hydrogenation of hydrozyls on the support (M-NO$^+$) and may ultimately lead to the formation of nitrogen gas.

It is important to note that these NOH species present the same behaviour as nitrozyls under the reaction conditions examined.

Fig. 6 presents the results of the influence of temperature on N-species adsorbed on 1 wt.% Pd-0.5 wt.% Cu/γ-Al$_2$O$_3$ (a) and 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ (b) catalysts after NO$_3^-$/H$_2$ (1) and NO$_3^-$/H$_2$/O$_2$ reactions (2), and temperature programmed desorption (TPD) under He at 25 °C. Spectra recorded in the 2400–1000 cm^{-1} range after 25, 50, 100, 300, 400, 500 °C under flow of He (TPD). The peaks in the IR spectra recorded for all the temperatures are practically in the same frequencies (2400–1000 cm^{-1}). As shown in Fig. 6, the strength of the bond of adsorbed N-species to the surface (as revealed by their desorption temperature) seems to be decreased in the following order: coordinated nitrates and chelating nitrites on support (1249 cm^{-1}), adsorbed nitrites on Pd (1638 cm^{-1}) (T > 200 °C) ≥ NOH, nitrates on support (1200–1000 cm^{-1}), nitrozyls (NO$^+$) on support (2098 cm^{-1}) (T = 150–200 °C) > ionic nitrates on Cu (1391 cm^{-1}) and adsorbed nitrites on support (1523 cm^{-1}) (T = 75–100 °C). The latter results are very important since they provide strong evidence that bond strength of the aforementioned N-species with the catalytic surface is significant affected both by the chemical composition of the support and the gas feed stream. It is highly important to note that, ionic nitrates on Cu and adsorbed nitrites on support appear to be the more loosely bonded species on the catalytic surface. In addition their bond strength was found to decrease further in the presence of TiO$_2$ in the support or O$_2$ in the gas feed stream. The latter results indicate that these species can be considered very labile and thus can easily spillover from Cu to either Pd or the support.

Figs. 7 and 8, present the results obtained by SSITKA-DRIFTS experiments over bimetallic Pd-Cu catalysts supported on Al$_2$O$_3$ and TiO$_2$-Al$_2$O$_3$ following NO$_3^-$/H$_2$ or NO$_3^-$/H$_2$/O$_2$ reaction at room temperature.

In particular, Fig. 7 presents the FTIR spectra recorded in the 2400–900 cm^{-1} range over the Pd-Cu/γ-Al$_2$O$_3$ catalyst before and after the isotopic switch from ^{14}NO$_3^-$/H$_2$ to ^{15}NO$_3^-$/H$_2$ (Fig. 7a) or from ^{14}NO$_3^-$/H$_2$/O$_2$ to ^{15}NO$_3^-$/H$_2$/O$_2$ (Fig. 7b). All spectra were processed following the necessary deconvolution analysis (OriginPro) and curve fitting. According to the SSITKA technique, the peaks that are shifted to lower wavenumbers after the isotopic switch from ^{14}NO$_3^-$ to ^{15}NO$_3^-$ correspond to active intermediate species of the reaction. As shown in Fig. 9a, three peaks appear to be shifted to lower wavenumbers when the feed composition was changed from ^{14}NO$_3^-$/H$_2$ to ^{15}NO$_3^-$/H$_2$. In particular, the shifted peaks correspond to linear NO on Pd (1702 → 1669 cm^{-1}), adsorbed nitrites on the support (1529 → 1507 cm^{-1}) and ionic nitrates on Cu cations (1402 → 1379 cm^{-1}). The latter active species are probably the first intermediate for the reduction of nitrates to nitrites on copper sites. Based on the above observations, the sequential reduction of NO$_3^-$$_{(ads)}$ into gaseous end products NH$_4^+$/N$_2$ takes place on different active sites of the catalyst surface (*Pd-Cu ensembles* – NO$_{3(ads)}$, *support* – NO$_{2(ads)}$, *monometallic Pd clusters* – NO$_{(ads)}$), indicating firstly that H$_2$ is easily dissociated on Pd particles and then spills over onto the Cu and the metal oxides (support), and secondly that NO$_{(ads)}$ is possibly diffused from support to adjusted Pd sites, for further reaction. In contrast, when oxygen was used in the reaction feed (Fig. 8b), nitrites were proven to be further reduced (NO) on Pd sites instead of the support. According to the results of Fig. 7b, the peaks that correspond to linear NO on Pd (1699 → 1670 cm^{-1}), adsorbed nitrites on Pd (1642 → 1604 cm^{-1}) and ionic nitrates on Cu cations (1403 → 1365 cm^{-1}) were shifted when the isotopic exchange (^{14}NO$_3^-$/H$_2$/O$_2$ to ^{15}NO$_3^-$/H$_2$/O$_2$) took place. Based on the above results, it is therefore concluded that the reduction of NO$_2^-$ to NO is favoured on partially oxidized Pd, only when adequate supply of oxygen is available. This could be probably due to the formation of Pd oxo-species which provide

Fig. 7. DRIFTS spectra recorded over the 1 wt.% Pd-0.5 wt.% Cu/γ-Al$_2$O$_3$ after 150 min of ^{14}NO$_3^-$/H$_2$ or ^{14}NO$_3^-$/H$_2$/O$_2$ reaction (▬) at 25 °C, and after 150 min following the isotopic switch ^{14}NO$_3^-$/H$_2$ or ^{14}NO$_3^-$/H$_2$/O$_2$ → ^{15}NO$_3^-$/H$_2$ or ^{15}NO$_3^-$/H$_2$/O$_2$ (—) at 25 °C. M: Metal cation on the support surface. Reaction conditions: Gas Feed Stream Composition = 100 vol.% H$_2$ or 80 vol.% H$_2$/20 vol.% air; TPD Flow Rate = 50 NmL/min; [NO$_3^-$]° = 75 mg/L; Liquid Flow Rate = 4 mL/min; W$_{cat}$ = 4 g; T = 25 °C; P = 1.2 atm.

additional sites for NO$_2^-$ adsorption. Moreover, taking into account the fact that the presence of oxygen enhances the reaction's selectivity towards N$_2$, one can safely state that adsorbed nitrites on Pd (in the form of linear NO or bidentate nitrates) sites lead selectively to the formation of N$_2$ rather than NH$_4^+$. As mentioned before, the identification of nitrates on Cu sites as active N-species of the reaction, confirms the high reactivity and involvement of Cu in the overall mechanism of the reaction The latter is in full agreement with the literature [1] where the reduction of NO$_3^-$ to NO$_2^-$ is almost solely attributed to the synergistic action between Pd and Cu sites, whereas the reduction of NO$_3^-$ to NO$_2^-$ is believed to take place on Cu, the latter being reduced by hydrogen species spilt over from Pd. It has been also reported that further reduction of NO$_2^-$ (through NO) towards NH$_4^+$ and N$_2$ takes place on Pd. However, the results of Fig. 8, provide strong evidence for the reduction of NO$_2^-$ to NO and further to N$_2$ on the support or metal-support interface (metal cation sites), instead of Pd metal surface. Recent studies report a possible involvement of the support to this first step of the reaction, i.e., reduction of nitrates to nitrites [8,58,64], a fact which is in agreement to the results of the present work.

Fig. 8 presents the FTIR spectra recorded in the 2400–900 cm^{-1} range over the Pd-Cu/Al$_2$O$_3$-TiO$_2$ catalyst before and after the isotopic switch from ^{14}NO$_3^-$/H$_2$ to ^{15}NO$_3^-$/H$_2$ (Fig. 8a) or from

(a)
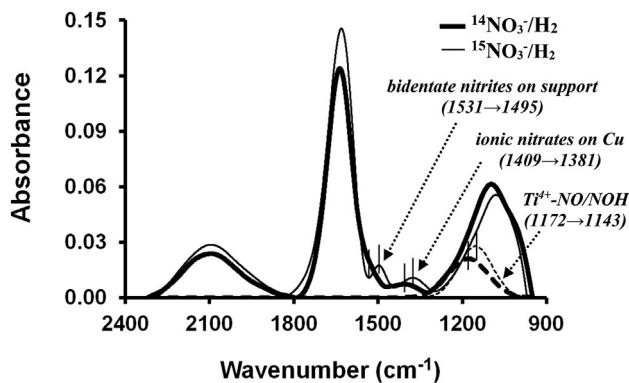
(b)
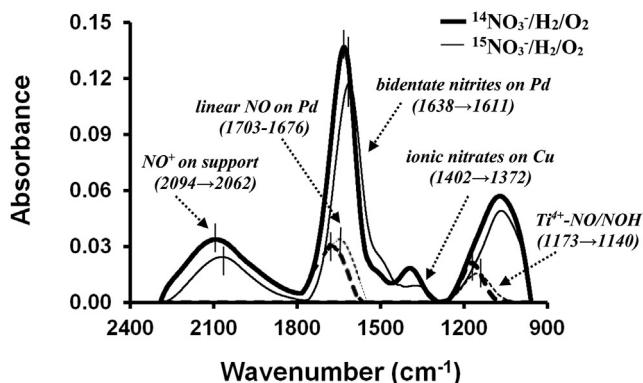
Fig. 8. DRIFTS spectra recorded over the 1 wt.% Pd-0.5 wt.% Cu/TiO$_2$-Al$_2$O$_3$ after 150 min of ^{14}NO$_3^-$/H$_2$ or ^{14}NO$_3^-$/H$_2$/O$_2$ reaction ($\blacksquare$) at 25 °C, and after 150 min following the isotopic switch ^{14}NO$_3^-$/H$_2$ or ^{14}NO$_3^-$/H$_2$/O$_2$ → ^{15}NO$_3^-$/H$_2$ or ^{15}NO$_3^-$/H$_2$/O$_2$ (—)at 25 °C. M: Metal cation on the support surface. Reaction conditions: Gas Feed Stream Composition = 100 vol.% H$_2$ or 80 vol.% H$_2$/20 vol.% air; TPD Flow Rate = 50 NmL/min; [NO$_3^-$]° = 75 mg/L; Liquid Flow Rate = 4 mL/min; W$_{cat}$ = 4 g; T = 25 °C; P = 1.2 atm.

NO$_3^-$/H$_2$/O$_2$ to ^{14}NO$_3^-$/H$_2$/O$_2$ (Fig. 8b). As shown in Fig. 8a, three active N-species, are also observed in the case of the Pd-Cu/Al$_2$O$_3$-TiO$_2$ catalyst during NO$_3^-$/H$_2$ reaction. In particular, adsorbed *nitrites* on the support *(1531 → 1495* cm^{-1}), ionic nitrates on Cu cations (*1409 → 1381* cm^{-1}), and NOH species on *Lewis* acid sites of titanium dioxide (Ti^{4+}-NO/NOH) (*1172 → 1143* cm^{-1}) are actually involved during subsequent reduction of nitrate to N$_2$ and NH$_4^+$. It should be noted at this point, that a possible fourth active species might be present in the range of 2000–2200 cm^{-1}, which could not be discriminated (even after deconvolution), due to the complexity of the band. Based on the above observations, both adsorption and reduction of NO$_2^-$ properly take place on the support surface (in the form of bidentate nitrates on Ti) leading to the formation of NO$_{(ads)}$ on TiO$_2$ (Ti^{4+}-NO or Ti^{4+}-NO$^+$), which in turns leads to enhanced N$_2$ production. Significant different FTIR spectra profile was observed over the latter catalyst, when oxygen was used in the reaction feed stream. As shown in Fig. 8b, five intermediate species were found to be involved in the reaction; ionic nitrates on the Cu cations (*1402 → 1372* cm^{-1}), adsorbed nitrites on Pd (*1638 → 1611* cm^{-1}), linear NO on Pd (*1703 → 1676* cm^{-1}), nitrozyls (NO$^+$) on the support (*2094 → 2062* cm^{-1}) and NOH on Lewis acid on the titanium dioxide (Ti^{4+}-NO/NOH) (*1173 → 1140* cm^{-1}). It can be clearly seen from the results presented in Figs. 8a and 8b, that adsorbed *nitrosyls (NO$^+$)* on the support were found to be active, in the case of Pd-Cu/Al$_2$O$_3$-TiO$_2$, only when oxygen is present in the reaction feed. The latter species can be considered as the intermedi-

ate active species selectively leading to the formation of N$_2$ instead of NH$_4^+$. The latter catalytic system exhibits greatly enhanced selectivity toward N$_2$, under oxidizing conditions, possibly due to the interaction between NO$_x$ species (e.g., Pd-NO/N, Ti^{4+}-NO/NO$^+$) at the metal-support interface.

These results clearly and conclusively demonstrate that the use of titanium dioxide (TiO$_2$) coated alumina spheres in the reaction under study, leads to the formation of two different active nitrogen containing species, which are located on the support (or the metal-support interface). The latter results confirm the crucial role of the support chemical composition on the overall mechanism of the reactions at hand. Taking into account the positive effect of titanium dioxide on the N$_2$-selectivity of the NO$_3^-$/H$_2$ (or NO$_3^-$/H$_2$/O$_2$) reaction, it can be safely stated that Ti^{4+}-NO/NOH species are active intermediates adsorbed on the support (TiO$_2$) probably leading to the production of N$_2$ via nitrozyls (NO$^+$) reduction pathway, rather than the formation of NH$_4^+$. The latter hypothesis is in a very good agreement with the results of Fig. 6b where the surface coverage of nitrozyls on the support was found to increase when TiO$_2$ was added to the support. Moreover, it is noteworthy that the presence of oxygen in the reaction exerted the same effect on adsorbed nitrites on Pd, as in the case of the Pd-Cu/γ-Al$_2$O$_3$ catalyst, while the identification of active nitrate ions on the Cu confirms for once more, the importance that Cu is involved on the reduction of nitrates to nitrites.

The surface acidity/basicity of the support is well known to affect the properties (especially reaction's selectivity) of supported catalysts for the reaction at hand. It is well documented that both metal oxides examined in the present work (Al$_2$O$_3$ and TiO$_2$) present basic and acidic sites. The target of the present work was not just to prove whether surface acidity affects (positively or negatively) the selectivity of the reaction, but to go a step beyond and prove why and how surface acidity affects the reaction's selectivity. The findings of the present work showed that TiO$_2$ offers specific Bronsted and Lewis acid sites for the formation of particular adsorbed species which were found to be active intermediate species of the reaction at hand (Table 1, Fig. 8), a result that was not observed in the case where pure Al$_2$O$_3$ was used as a support. The latter result indicates that surface acidity favors reaction's selectivity by offering "unique" sites for the formation of active intermediate species.

As has been previously discussed, several adsorbed N-species on the support show high reactivity with hydrogen. The results from the isotopic experiments are extremely useful since they reveal that only a small portion of the intermediate N-species, that are formed on the catalytic surface during reaction conditions, are active and react to produce the final products (N$_2$ and NH$_4^+$). The adsorbed N-species that showed the highest reactivity with H$_2$ (DRIFTS) have been identified as active species (DRIFTS-SSITKA) for both Pd-Cu/γ-Al$_2$O$_3$ and Pd-Cu/TiO$_2$-Al$_2$O$_3$. Based on the above, it can be clearly claimed that at least two active species are located on the support. Since hydrogen molecule can only be dissociated on Pd metal, it is reasonable to expect that a hydrogen spillover mechanism (from Pd to the support) must be involved. Ionic nitrates on Cu (1395 cm^{-1}) showed the greater reactivity with hydrogen. This is confirmed from the SSITKA results, according to which these species are active for both catalysts under any reaction conditions examined. In addition, adsorbed nitrites on the Pd (1640 cm^{-1}) were found to be active only in the presence of oxygen (80 vol.% H$_2$/4.2 vol.% O$_2$) in the gas feed, whereas adsorbed nitrites on the support (1531 cm^{-1}) are active only in the case of NO$_3^-$/H$_2$ reaction. Consequently, oxygen acts as a promoter of the reduction of the adsorbed nitrites on the Pd rather than on the support. It could be suggested that the main reasons that lead to the improvement of the N$_2$ selectivity of the NO$_3^-$/H$_2$ reaction in the presence of oxygen in the gas feed stream might be the ability of oxygen to regulate the hydrogen coverage on the metal surface

(Pd and/or Cu and/or Pd-Cu), and also the oxidation state of the metallic phase/s towards an increase of N_2 selectivity. The fact that Pd-Cu/γ-Al$_2$O$_3$ and Pd-Cu/TiO$_2$-Al$_2$O$_3$ show greater conversion values for NO$_3^-$, as well as reduced selectivity values towards NH$_4^+$ in the presence of oxygen in the gas feed (80 vol.% H$_2$/4.2 vol.% O$_2$), suggests that adsorbed nitrites on the support (1529 cm^{-1}) are reduced selectively to NH$_4^+$, whereas adsorbed nitrites on the Pd (1640 cm^{-1}) are reduced selectively to N_2. Linear NO on Pd ($\sim$1702 cm^{-1}) was proved to be an active species, except in the case of Pd-Cu/TiO$_2$-Al$_2$O$_3$ (NO$_3^-$/H$_2$ reaction conditions), whereas NOH (1169 cm^{-1}) only on the Pd-Cu/TiO$_2$-Al$_2$O$_3$. The adsorbed nitrozyls (NO$^+$) on the support (2094 cm^{-1}) appear as active species only in the case of Pd-Cu/TiO$_2$-Al$_2$O$_3$ catalyst, only under NO$_3^-$/H$_2$/O$_2$ reaction conditions. The increased selectivity towards N_2 that was observed in the case of Pd-Cu/TiO$_2$-Al$_2$O$_3$ under NO$_3^-$/H$_2$/O$_2$ reaction conditions leads to the conclusion that adsorbed NO$^+$ species on TiO$_2$ probably lead to N_2, as well. Therefore, the excellent contact between TiO$_2$ and Pd phases is expected to have a positive effect on the catalytic properties of the supported catalyst under question, by providing ideal conditions for the formation and interaction of the right species. The reduction of adsorbed NO on Pd is claimed to be the rate determining step that is playing a key role on the selectivity of the reaction. Based on the fact that hydrogen is chemisorbed only on metal surfaces (e.g. Pd) and not on metal oxides (e.g. TiO$_2$-Al$_2$O$_3$) [57,59], it is expected that the reduction of the NO proceeds only in the case where NO is adsorbed on Pd. However, SSITKA-DRIFTS results proved that NO, which is formed as an active intermediate species via NO$_3^-$/H$_2$/O$_2$ reaction over Pd-Cu/TiO$_2$-Al$_2$O$_3$ catalyst, was found to be on the support (M-NO$^{\delta+}$). Recent SSITKA-MS experiments conducted over the present catalysts, have proven the existence of such a spillover mechanism (atomic hydrogen is diffused through spill over from the Pd to nearby support sites) under the experimental conditions examined [15]. Moreover, several results have been reported over supported-metal catalysts, that provide significant evidence for the existence of such a mechanism, both for the reduction of nitrates with hydrogen in aqueous media [47], as well as for the reduction of nitric oxide with hydrogen [65,66]. The addition of titanium oxide to the support system of the present catalyst is expected to significantly increase the quality of the contact between the metal and the support, as a result of the strong interaction of the metallic clusters (Pd, Cu, Pd-Cu) with the oxidized Titanium cations (Ti^{3+}). The interaction of noble metals with oxidized titanium cations (Ti^{3+}) is a well-known phenomenon and falls in the category of Strong Metal-Support Interactions (SMSI) [60,67,68].

4. Conclusions

The present work provides fundamental mechanistic information for the NO$_3^-$/H$_2$/O$_2$ reaction over supported Pd-Cu catalysts. This study was undertaken in order to provide information concerning the N-pathways of the reaction at hand. The elucidation of the intrinsic reasons that led to the remarkable catalytic behavior (activity and selectivity) of the Pd-Cu/TiO$_2$-Al$_2$O$_3$ system, especially when oxygen is present in the gas feed stream, was the main scope of the current work. Experiments revealed that the mechanism of N_2 production strongly depends on the nature of the support and the presence of O$_2$ (air) in the reaction. In particular, these parameters were found to significantly affect the formation of different adsorbed active intermediate N-species on the support or metal surface. In more detail, the present study reveals several similarities and differences on N-species as follows:

i Inactive adsorbed N-species were also found to accumulate on metal and support surface.

ii The formation of *active* adsorbed *N-species* depends on both the chemical composition of the support and reaction conditions.

iii Adsorbed *ionic nitrates on Cu* were found to be active on both catalysts under any reaction conditions.

iv Adsorbed *nitrites on Pd sites (actually they are nitrates which were formed after adsorption of nitrites on the partially oxidized surface of Pd)* were found to be active only when oxygen was present in the feed stream for both catalysts.

v Adsorbed *nitrites on the support* were determined to be active species for the NO$_3^-$/H$_2$ reaction over Pd-Cu/γ-Al$_2$O$_3$ and Pd-Cu/TiO$_2$-Al$_2$O$_3$ catalysts.

vi *Active adsorbed NO on the support* was proved to spill over to Pd sites for further reaction, only in the absence of TiO$_2$ in the support and oxygen in the feed stream.

vii *Linear NO on Pd* was found to be an active species in all cases with exception of NO$_3^-$/H$_2$ reaction over Pd-Cu/TiO$_2$-Al$_2$O$_3$.

viii *Adsorbed nitrosyls (NO$^+$) on the support (actually they are NO adsorbed on Lewis acid sites of TiO$_2$)* were found to be active only in the case of the NO$_3^-$/H$_2$/O$_2$ reaction over Pd-Cu/TiO$_2$-Al$_2$O$_3$. The latter species *(Ti^{4+}-NO)* can be considered as the intermediate active species selectively leading to the formation of N_2 instead of NH$_4^+$. The concurrent presence of active NO$_x$ species on the metal and support surface, of the most selective catalytic system, indicates that the formation of N_2 might require the interaction of two different types of adsorbed NO$_x$ species.

Conclusively, the present work provides solid mechanistic evidence for the involvement of support and bimetallic crystallites (PdCu) in the overall reaction mechanism and the presence of a hydrogen spillover process towards the periphery of metal (Pd) – support and metal (Pd) – metal (Cu) interface. In particular, the presence of active N-species (e.g, Ti^{4+}-NO$^+$ and Ti^{4+}-NO) on titanium dioxide, indicates that atomic hydrogen is diffused from Pd to the support via a hydrogen spillover process, promoting the reduction of nitrites. In addition, this study provides incontrovertible evidence that Cu clusters appear as active sites for the reduction of nitrates. In this case, hydrogen is dissociated on Pd, and migrated (spill over) onto the Cu sites of bimetallic Pd-Cu clusters activating the reduction of nitrates, thus indicating a strong bimetal Pd-Cu interaction. Furthermore, nitrites were found to be active on Pd only when oxygen was present in the feed, probably due to the higher oxidation state of Pd, which might favor the adsorption of NO$_2^-$ and the presence of Pd oxo-species which provide additional sites for NO$_2^-$ adsorption.

The results of the present work indicate that the selectivity of the reaction towards N_2 is highly affected by two major key-factors, i.e., the M-NO bond strength (where M = Pd or metal cation of the support) and hydrogen surface coverage. It was proven that the formation of N_2 requires a specific M-NO bond strength and a moderate hydrogen surface coverage. Both latter key-parameters can be adjusted by the support and feed chemical composition.

References

[1] N. Barrabes, J. Just, A. Dafinov, F. Medina, J.L.G. Fierro, J.E. Sueiras, P. Salagre, Y. Cesteros, Appl. Catal. B: Environ. 62 (2006) 77–85.
[2] O.S.G.P. Soares, J.J.M. Órfão, J. Ruiz-Martínez, J. Silvestre-Albero, A. Sepúlveda-Escribano, M.F.R. Pereira, Chem. Eng. J. 165 (2010) 78–88.
[3] S. Hörold, K.D. Vorlop, T. Tacke, M. Sell, Catal. Today 17 (1993) 21–30.
[4] L. Lemaignen, C. Tong, V. Begon, R. Burch, D. Chadwick, Catal. Today 75 (2002) 43–48.
[5] Y. Wang, J. Qu, H. Liu, J. Mol. Catal. A 272 (2007) 31–37.
[6] R. Zhang, D. Shuai, K.A. Guy, J.R. Shapley, T.J. Strathmann, C.J. Werth, ChemCatChem 5 (2013) 313–321.
[7] S.D. Ebbesen, B.L. Mojet, L. Lefferts, Phys. Chem. C 115 (4) (2011) 1186–1194.
[8] J. Sa, J. Anderson, Appl. Catal. B: Environ. 77 (2008) 409–417.
[9] I. Mikami, Y. Sakamoto, Y. Yoshinaga, T. Okuhara, Appl. Catal. B: Environ. 44 (2003) 79–86.
[10] K. Tanaka, M. Ikai, Catal 20 (2002) 25–33.

[11] K. Rahkamaa, T. Salmi, R. Keiski, J. Wärnå, Y. Zhou, Chem. Eng. Sci. 56 (2001) 1395–1401.
[12] A. Obuchi, S. Naito, T. Onishi, K. Tamaru, Surf. Sci. 122 (1982) 235–255.
[13] I. Matsuo, J. Nakamura, H. Hirano, K. Yamada, K. Tamaru, J. Phys. Chem. 93 (1989) 7747–7749.
[14] T. Yamada, K. Tanaka, J. Am. Chem. Soc. 111 (1989) 6880–6881.
[15] C.P. Theologides, P.G. Savva, G.G. Olympiou, N.A. Pantelidou, B.K. Constantinou, V.K. Chatziiona, L.Y. Valanidou, C.T. Piscopianou, C.N. Costa, Water Sci. Technol. 69 (2013) 680.
[16] C.P. Theologides, P.G. Savva, C.N. Costa, Appl. Catal. B: Environ. 102 (2011) 54–61.
[17] C.P. Theologides, P.G. Savva, G.G. Olympiou, N.A. Pantelidou, B.K. Constantinou, V.K. Chatziiona, L.Y. Valanidou, C.T. Piscopianou, C.N. Costa, Water Sci. Technol. 68 (2013) 2309–2315.
[18] C.D. DiGiulio, V.G. Komvokis, M.D. Amiridis, Catal. Today 184 (2012) 8–19.
[19] S. Morandi, F. Prinetto, L. Castoldi, L. Lietti, P. Forzatti, G. Ghiotti, Phys. Chem. Chem. Phys. 15 (2013) 13409–13417.
[20] S. Tamás, J.H. Kwak, D.H. Kim, J.C. Hanson, C.H.F. Peden, J. Szanyi, J. Catal, (2006) 51–64.
[21] A. Pintar, J. Batista, J. Hazard. Mater. 149 (2007) 387–398.
[22] S.J. Huang, A.B. Walters, M.A. Vannice, J. Catal. 173 (1998) 229–237.
[23] K.I. Hadjiivanov, Catal. Rev. Sci. Eng. 42 (2000) 71–144.
[24] G. Ramis, F. Bregani, P. Forzatti, Appl. Catal. 64 (1990) 259–278.
[25] K. Hadjiivanov, V. Bushev, M. Kantcheva, D. Klissurski, Langmuir 10 (1994) 464–471.
[26] T.E. Hoost, K. Otto, K.A. Laframboise, J. Catal. 155 (1995) 303–311.
[27] P.J. Levy, V. Pitchon, V. Perrichon, M. Primet, M. Chevrier, C. Gauthier, J. Catal. 178 (1998) 363–371.
[28] E. Rogemond, N. Essayem, R. Frety, V. Perrichon, M. Primet, M. Chevrier, C. Gauthier, F. Mathis, J. Catal. 186 (1999) 414–422.
[29] Z. Liu, P. Millington, J.E. Ballie, R. Rajaram, J.A. Anderson, Micropor. Mesopor. Mater. 104 (2007) 159–170.
[30] O.S. Alexeev, S. Krishnamoorthy, M.S. Ziebarth, G. Yaluris, T.G. Roberie, M.D. Amiridis, Catal. Today 127 (2007) 176–188.
[31] D.K. Paul, B.W. Smithl, C.D. Marten, J. Burchett, J. Mol. Catal. A 167 (2001) 67–79.
[32] K. Almusaiteer, S.S.C. Chuang, J. Catal. 184 (1999) 189–201.
[33] R. Raval, G. Blyholder, S. Haq, D.A. King, J. Phys, Condens. Matter. 1 (1989) 165–169.
[34] S.W. Jorgensen, N.D.S. Canning, R.J. Madix, Surf. Sci. 179 (1987) 322–350.
[35] C. Hess, E. Ozensoy, D.W. Goodman, J. Phys. Chem. B 107 (2003) 2759–2764.
[36] X. Xu, P. Chen, D.W. Goodman, J. Phys. Chem. 98 (1994) 9242–9246.
[37] C.A. Rice, S.D. Worley, C.W. Curtis, J.A. Guin, A.R. Tarrer, J. Chem. Phys. 74 (1981) 6487–6497.
[38] M. Kantcheva, J. Catal. 204 (2001) 479–494.
[39] E.A. Hyde, R. Rudham, C.H. Rochester, J. Chem. Soc. Faraday Trans. 80 (1984) 531–541.
[40] J. Liang, H.P. Wang, L.D. Spicer, J. Phys. Chem. 89 (1985) 5840–5845.
[41] Y. Chi, S.S.C. Chuang, Catal. Today 62 (2000) 303–318.
[42] D. Pozdnyakov, V. Filimonov, Kinet. Katal. 14 (1973) 760–766.
[43] G. Ramis, G. Busca, V. Lorenzelli, P. Forzatti, Appl. Catal. 64 (1990) 243–257.
[44] S. Suarez, S.M. Jung, P. Avila, P. Grange, J. Blanco, Catal. Today 75 (2002) 331–338.
[45] H. Schneider, S. Tschudin, M. Schneider, A. Wokaun, A. Baiker, J. Catal. 147 (1994) 5–14.
[46] S.-J. Huang, A.B. Walters, M.A. Vannice, Catal. Lett. 64 (2000) 77–83.
[47] C.N. Costa, PhD Thesis, University of Cyprus, 2003.
[48] P. Stoltze, Introduction to Heterogeneous Catalysis, Aalborg University, 2000.
[49] K. Yokota, M. Fukui, T. Tanaka, Appl. Surf. Sci. 121–122 (1997) 273–277.
[50] J. Sa, J. Montero, E. Duncan, J.A. Anderson, Appl. Catal. B: Environ. 73 (2007) 98–105.
[51] F. Epron, F. Gauthard, C. Pineda, J. Barbier, J. Catal. 198 (2001) 309–318.
[52] J. Sa, H. Vinek, Appl. Catal. B: Environ. 57 (4) (2005) 247–256.
[53] A. Rochefort, M. Abon, P. Deliche're, J.C. Bertolini, Surf. Sci. 294 (1993) 43–52.
[54] C.A. Leon y Leon, M.A. Vannice, Appl. Catal. 69 (1991) 291–304.
[55] C.A. LeonyLeon, M.A. Vannice, Appl. Catal. 69 (1991) 269–436.
[56] A. Mönnich, Ph.D. Thesis, University Oldenburg, Germany, 2000.
[57] H. Berndt, I. Mönnich, B. Lücke, M. Menzel, Appl. Catal. B: Environ. 30 (2001) 111–122.
[58] J. Sá, T. Berger, K. Föttinger, A. Riss, J. Anderson, H. Vinek, J. Catal. 234 (2005) 282–291.
[59] R. Gavagnin, L. Biasetto, F. Pinna, G. Strukul, Appl. Catal. B: Environ. 38 (2002) 91–99.
[60] F. Epron, F. Gauthard, J. Barbier, J. Catal. 206 (2002) 363–367.
[61] C.N. Costa, A.M. Efstathiou, J. Phys. Chem. C 111 (2007) 3010–3020.
[62] P.G. Savva, A.M. Efstathiou, J. Catal. 257 (2008) 324–333.
[63] A. Ghorbel, M.J. Primet, Chem. Phys. 73 (1976) 1.
[64] I. Dodouche, D.P. Barbosa, M.G. Rangel, F. Epron, Appl. Catal. B: Environ. 93 (2009) 50–55.
[65] M. D'Arino, F. Pinna, G. Strukul, Appl. Catal. B: Environ. 53 (2004) 161–168.
[66] P.G. Savva, G.G. Olympiou, C.N. Costa, V.A. Ryzhkov, A.M. Efstathiou, Catal. Today 102–103 (2005) 78–84.
[67] D.E. Resasco, G.L. Haller, J. Catal. 82 (1983) 279–288.
[68] K.D. Fliatoura, X.E. Verykios, C.N. Costa, A.M. Efstathiou, J. Catal. 183 (1999) 323–335.